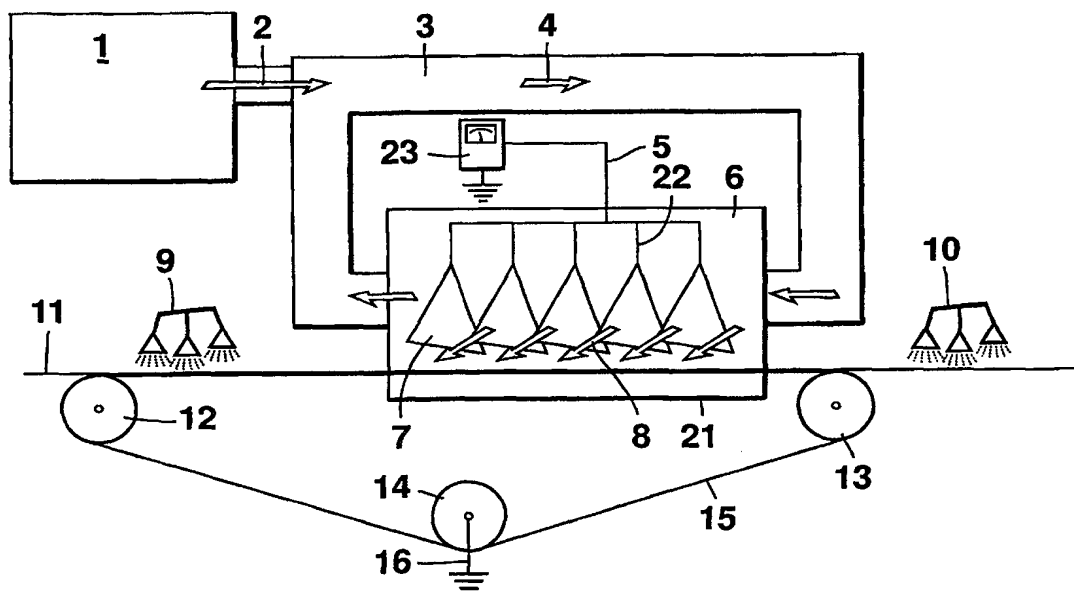




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>D21H 17/67, 19/36, 23/22</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/03092</b> <b>(43) International Publication Date:</b> 20 January 2000 (20.01.00)
<b>(21) International Application Number:</b> PCT/FI99/00604 <b>(22) International Filing Date:</b> 7 July 1999 (07.07.99) <b>(30) Priority Data:</b> 981574 8 July 1998 (08.07.98) FI <b>(71) Applicant (for all designated States except US):</b> VALMET CORPORATION [FI/FI]; Panuntie 6, FIN-00620 Helsinki (FI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> NISSINEN, Vilho [FI/FI]; Onkimaantie 195, FIN-04660 Numminen (FI). NYBERG, Timo [FI/FI]; Koivuviita 12 B 6, FIN-02130 Espoo (FI). RAJALA, Pasi [FI/FI]; Pajalantie 35 B 20, FIN-04400 Järvenpää (FI). GRÖNROOS, Lars [FI/FI]; Simolankatu 7 E 2, FIN-33270 Tampere (FI). VIRTANEN, Pentti [FI/FI]; Köysiö 238, FIN-37800 Toijala (FI). KÄSMÄ, Veli [FI/FI]; Vääränkoivuntie 2 as. 35, FIN-37630 Valkeakoski (FI). NIEMELÄ, Hannu [FI/FI]; Sarvijaakonkatu 18 A 4, FIN-33540 Tampere (FI). <b>(74) Agent:</b> SEPPO LAINE OY; Itämerenkatu 3 B, FIN-00180 Helsinki (FI).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). <b>Published</b> <i>With international search report.</i>

**(54) Title:** METHOD FOR MAKING PAPER, ASSEMBLY FOR IMPLEMENTING THE METHOD AND PAPER PRODUCT PRODUCED BY THE METHOD

**(57) Abstract**

Method and assembly for forming a paper or board web and a product made using the method. According to the method, the web (11) is made from fibers and then the web (11) is treated with pigment particles. The web is treated with microscopic pigment particles whose average size is so small as to permit the particles to adhere to each other by van der Waals forces. The particles are transferred to the web and adhered thereto advantageously using an ion-blast technique.

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

**Method for making paper, assembly for implementing the  
method and paper product produced by the method**

5 The invention relates to method according to the preamble  
of claim 1 for manufacturing coated paper, board or  
similar product having a plant fiber base, in which  
method a layer of coating furnish is applied and adhered  
to a base web made of the fibers. The coating furnish at  
10 least partially consists of a carbonate compound.

The invention also relates to an assembly suitable for  
implementing said method and a plant-fiber-based product  
coated with said carbonate-based coating furnish.

15

In the context of the present application, the term paper  
is used when reference is made to any product produced on  
a plant fiber base such as a web of paper or board.

20 Generally, webs of paper and board are coated in order to  
enhance their printability properties. Among other  
things, the purpose of the coating is to improve the  
smoothness and whiteness of the base web and, particular-  
ly with thin base webs, to increase the opacity of the  
25 web material. Conventionally, the coating is applied to  
the base web surface as an aqueous suspension. There may  
be applied a plurality of coat layers and the application  
of the coat layers can be accomplished using a number of  
different methods. Since all the conventional methods  
30 apply the coating as an aqueous suspension, the drying of  
the coat forms a massive step in the coating process.  
Drying of the coat is an energy-intensive process and the  
drying of a fast moving web needs a long dryer section in  
order to direct a sufficient amount of drying energy to  
35 the web. Also the routing of the web to be processed is  
difficult, because the web cannot be guided by any  
members contacting it from its wet side until the coating

has become adequately dry.

It is an object of the present invention to overcome the disadvantages of the above-described technology and to  
5 provide an entirely novel type of application method for coating a paper web.

The goal of the invention is achieved by forming the coating from microparticulate calcium carbonate or pre-  
10 cursors thereof, said microparticulate coating being transferred to the web in dry form or as a suspension of a high solids content.

More specifically, the method according to the invention  
15 is characterized by what is stated in the characterizing part of claim 1.

Further, the assembly according to the invention is characterized by what is stated in the characterizing  
20 part of claim 38.

Still further, the paper web product according to the invention is characterized by what is stated in the characterizing part of claim 55.

25

The invention offers significant benefits.

By virtue of the invention, a web can be coated without using any water in the coating furnish, whereby also the  
30 web need not be dried during any step of the coating process and no equipment is required for preparing an aqueous coating mix. The overall length of the coater can be made shorter and its construction may be simplified. Because a major fraction of the energy consumed at the  
35 coater is used for drying the aqueous coating suspension, the invention offers significant savings in the specific energy consumption of coated paper grades. The invention

may be combined with a dry base web-formation method (cf. FI Pat. Appl. No. 973775 filed by the applicant), thus permitting the entire papermaking process to be carried out without any drying steps or, alternatively, using a minimal amount of water and drying. During web formation, calcium carbonate or its precursors can be fed into the fiber mass, whereby also the filler is introduced into the web. As known, calcium carbonate particles or the formation thereof in the web improves the interfiber bonding, whereby the web becomes stronger than a web containing no fillers.

By virtue of the invention, the paper surface can be provided with a coat of superior hiding power and smoothness. This kind of paper offers excellent printability. Moreover, coat defects such as streaking, orange peel patterning, uncoated patches and the like typically occurring in conjunction with blade, film-transfer and other known coating methods are eliminated. The dust of coating material can be effectively adhered to the web, whereby the soiling of the operating environment and equipment is smaller than with conventional wet coating methods. The method can be combined with known coating methods, thus permitting a dry coating to be applied on a wet coat and *vice versa*. The method can cost-effectively produce thick coats, because there is no need for intermediate drying between the application of successive coat layers and the thickness of a coat layer is limited only by the adherence of the coating to the web surface. To obtain heavy coat weights, it may be necessary to use binders that are applied to the web simultaneously with the coating or, during a separate step, under or over the coat. The calcium carbonate particles can be prepared in a separate process or coating equipment, or even directly onto the web.

In the following the invention will be examined in

greater detail with the help of exemplifying embodiments illustrated in the appended drawings in which

5 Figure 1 shows a first embodiment according to the invention;

Figure 2 shows a second embodiment according to the invention;

10 Figure 3 shows a third embodiment according to the invention;

Figure 4 shows a fourth embodiment according to the invention;

15 Figure 5 shows a fifth embodiment according to the invention;

20 Figure 6 shows a sixth embodiment according to the invention;

Figure 7 shows a seventh embodiment according to the invention; and

25 Figure 8 shows an eighth embodiment according to the invention.

Int. Pat. publication WO/96/237228 and FI Pat. Appl. 964,365 describe a method for preparing extremely small  
30 and homogeneously sized PCC (Precipitated Calcium Carbonate) particles. In this method, PCC particles are formed from slaked lime CaO with the help of water and carbon dioxide in a direct gas-phase reaction, whereby extremely small particles are created with a diameter  
35 smaller than 100 nm, even smaller than 20 nm. There is also described a method for coating particles of natural calcium carbonate with precipitated carbonate. Under

suitable conditions, the prepared elementary particles  
floc into roundish aggregate particles of a cloudberry  
shape that have better rheological and optical properties  
than conventional PCC particles of needle-like shape. The  
5 size distribution of the flocced aggregate particles is  
very narrow and the flocced particles made using this  
technique are almost invariably smaller than 500 nm. The  
particles forming the aggregates are bonded to each other  
by van der Waals and capillary forces that become  
10 effective when the particles are disposed from each other  
at a distance smaller than 100 nm. On the other hand, the  
zeta-potential that characterizes the potential  
difference of the particle's ion field to the medium  
tends to separate the particles from agglomerating with  
15 each other. As the zeta-potential is strongly dependent  
on the pH of the particle, the formation and size of the  
aggregate particles can be affected by varying the degree  
of turbulence, or average mutual distance, and pH of the  
particles tending to aggregate together. If the degree of  
20 turbulence in the particle flow is sufficiently high, the  
elementary particles can be kept apart from each other. A  
more detailed description is given in cited patent  
applications.

25 In the most advantageous embodiment of the invention, the  
use of PCC made using the novel technique is combined  
with application to a web by means of ion-blasting. Thus,  
when PCC is transferred, e.g., by ion-blasting to the web  
surface, the particles are bonded directly to each other  
30 and the web surface by van der Waals and other forces  
even without using any additional binder. Resultingly,  
the web is coated with a homogeneous and hiding layer of  
carbonate particles that has the same toughness as the  
single carbonate aggregates even though it smoothly  
35 covers the entire web of fibers. Coat application may  
also be accomplished using a gas flow, whereby a flow is  
directed tangential to the web surface performs so as to

smooth away the irregularities of the web surface when the particulate matter coating accumulates in the depressed points of the web in the same manner as drifting snow. The carbonate particles may also be impinged with a high velocity perpendicular to the web, whereby the carbonate particles are penetrated into the interstitial spaces between the web fibers thus introducing a filler into the base web. By virtue of this technique, the web-formation section of a paper machine can be constructed without a filler feed system.

Slaked lime and/or calcium hydroxide can be transferred to the web surface, e.g., at the press section of the paper machine by gas flow or, alternatively, by ion-blasting. Subsequently, the calcium oxide is let to react with water fog, liquid water or steam to form calcium hydroxide, after which the web is taken to a carbon dioxide atmosphere and there the reaction is continued forming calcium carbonate on the web surface, wherein the carbonate particles thus formed adhere to the web. When the method is combined with dry formation of the base web, the calcium oxide or calcium hydroxide can be introduced as one constituent of the web and then reacted into calcium carbonate. Herein, the web dry-forming step can be performed so that into the formed web of fibers are introduced nano-size particles of calcium carbonate that in the mix of fibers bond the fibers and particles into a strong web. Thus, it is possible to form a web entirely from a dry furnish and, furthermore, to replace a fraction of the fibrous raw material with calcium carbonate, whereby the amount of fibrous raw material can be reduced to a minimum from that customarily required in a finished web.

An important feature of the invention is the possibility of recycling the calcium carbonate of deinked waste paper by feeding the precipitated calcium carbonate of the



deinking process to a calcination plant. The calcium  
oxide obtained from the calcination plant can be treated  
into precipitated calcium carbonate that may then be used  
in the manner described cited publications and the  
5 present application.

The present application utilizes the so-called ion-blast  
technique. This technique is based on forming a strong  
electric field, between one or typically a plurality of  
10 pointed electrodes and one planar counterelectrode. The  
tip of the pointed electrode emits a corona discharge  
that charges particles located in the vicinity of the  
electrode tip thus causing the generation of ions in the  
electronegative gaseous medium. The ions migrate along  
15 the field lines extending between the electrode and the  
counterelectrode which is taken to the ground potential  
or to a lower potential, whereby the ions adhere to par-  
ticles they meet on their travel. The electric field  
transports the charged particles over the interelectrode  
20 gap toward the ground-potential electrode, where they  
attach to the substrate by electric and mechanical  
forces. If the distance between the opposed electrodes is  
large and the applied voltage is high (more than 50 kV),  
a gas flow is established between the opposed electrodes  
25 that mechanically transports the charged particles toward  
the ground potential. This flow is conventionally known  
as ion blast. In the ion-blast phenomenon, the electric  
field exiting from the tip of the electrode forms a  
conical field pattern in which the ionized gas and  
30 charged particles move. Ion blast can transport both  
solid particles and liquid droplets.

In papermaking, the ion-blast technique can be utilized  
for binding a raw material to a web-formation substrate  
35 or for transferring and adhering the coating to the sur-  
face of a paper or board web. Basically, the substrate  
can be any surface permissive to the electric field or,

alternatively, an electrically conducting surface. As the web in a continuous process must be formed on a moving surface, the web-formation substrate conventionally is a wire, felt or belt. In principle, the dryer the raw material of the web the smoother the surface can be on which the web is formed. In coat application, the formation substrate is the surface of a paper or board web.

In Fig. 1 is shown one embodiment of the invention. The calcium carbonate particles are here formed directly in a gas phase in a chamber 1 as described in above-cited patent applications and are taken therefrom via a tube 2 into a particle circulation path 3 formed by a circular tube. In the particle circulation, there is maintained a continuous flow (denoted by arrow 4) serving to keep the particles in a continuous motion and preventing their floccing into excessive large aggregates. Additionally, floccing can be controlled by altering the pH of the particulate matter fed into the circulation, whereby the zeta-potential of the particles is lowered and the floccing tendency is reduced. Correspondingly, the aggregate size can be increased by elevating the pH level of the particles. The particle circulation tube 3 is passed to an ion-blast zone 6 formed into a chamber 21. Via the chamber 21 is also passed a paper or board web 11 to be coated, as well as a conducting wire 15 supporting the same. In Fig. 1, the web is shown travelling from the left to the right. The wire 15 passes over guide rolls 12, 13, 14 so as to form an endless loop. The wire 15 is grounded or taken to a low potential via a connection 16 made to a guide roll 14, for instance.

To the interior of the ion-blast chamber 21 and directed toward the web 11 and the wire 15, there are adapted a plurality of pointed-tip electrodes 22 connected via a conductor 5 to a power supply 23. From the power supply, a high potential relative to the conducting wire 15 is

applied to the electrodes 22, whereby between the electrodes and the wire is created an ion-blast zone 7 of conical flux tubes of the electrical field that directs the particulate matter flow toward the web 11. As the field lines leaving the tip of each pointed electrode 22 form a flux tube of a conical shape, the number and location of electrode tips must be configured so that the conical flux tubes leaving the staggered electrode tips provide a uniform field on the surface of the web 11. The applied electrode voltage is dependent on the distance between the counterelectrode formed by the conducting wire 15 and electrode tips 22 that may be varied from 2 mm to 2 m; however, to keep the space requirements of the coating furnish feed equipment within practicable limits, an interelectrode distance range of 100 - 1000 mm is favoured. While a large interelectrode distance as such does not impair the function of the apparatus, it increases the external dimensions of the system and complicates the behaved control of material flows in the chamber 16. When using a design based on the practicably most favourable interelectrode distance range, the voltage applied between the opposed electrodes is typically set in the range 80 - 160 kV, but may be varied as widely as from 30 kV to 1000 kV. The counterelectrode may be run positive or negative, and the electrode tips may respectively be connected to the negative or positive terminal of the power supply.

As the particle flow fluidized by the carrier gas is continuously circulated via the chamber 21, the direction of the particle flow is affected by the velocity vector of the circulation and, hence, the direction of the particle path is incident on the web in the reverse direction to the travel of the web 11 as indicated by arrow 8 in the diagram. When the particles hit the surface of the web 11, they are brought to a close distance from each other and the fibers of the web, whereby they become

attached to the fibers and each other due to van der  
Waals and other forces, thus forming a tight and uniform  
layer of coating. Furthermore, the particle flow which is  
blasted obliquely against the travel of the web surface  
5 accumulates calcium carbonate particles in the depressed  
points of the web surface, whereby the profile of the  
coated surface becomes smoother. The adhering capability  
of the particles can be further improved by treating the  
web 11 with water or chemicals sprayed thereon prior to  
10 its entry in the ion-blast chamber. As known, water esta-  
blishes hydrogen bonds between the fibers of the paper  
web and also improves the bonding of the calcium car-  
bonate particles to the fibers and to each other. The  
coated web 11 may be further treated by a binding agent,  
15 water or chemicals sprayed from nozzles 10 located after  
the ion-blast chamber 21. It must be noted that the  
amount of water used in the method according to the in-  
vention is very minimal as compared with methods based on  
applying the coating as an aqueous suspension to the web.  
20 Hence, the need for high-capacity dryers is eliminated.

The ion-blast apparatus may under some conditions act as  
a capacitor that accumulates an electric charge, whereby  
the forces adhering the web to the conducting wire become  
25 unwieldy after the web has exited from under the counter-  
electrode. To discharge such adhering forces, a positive-  
or negative-potential corona discharge treatment 18 shown  
in Fig. 2 can be applied downstream from the web-forma-  
tion section. Instead of having a pointed tip, the elec-  
30 trodes 22 of the ion-blast apparatus may be planar or  
rail electrodes, and respectively, the counterelectrode  
need not necessarily be taken to the ground potential  
with the provision that its potential must obviously be  
lower than that of the corona-discharge-emitting  
35 electrodes. Also the ion-blast chamber 21 may be preceded  
by a corona discharge device 17 serving to bring the web  
surface to a suitable potential and to adhere the web to

the conducting wire at the meeting point of the web with the wire.

The bonding strength of the coating to the web fibers may also be enhanced by a mechanical or thermal treatment or a combination thereof as shown in Fig. 3. In this configuration, on the travel of the web after the ion-blast chamber 21 there is arranged a pair of rolls 19 having the web 11 being treated passing through the compressive nip between the rolls. Since the web is practically dry, it can be passed directly into the nip of the compressive rolls. The rolls 19 may be, e.g., of the same type as the rolls used in calenders and the web finishing treatment can be performed using force levels equivalent to those used in calendering, thus permitting the finished web surface to receive gloss simultaneously with gaining an improved adherence of the coat. In conjunction with a surface treatment similar to calendering, it is advantageous to control the web moisture content to a proper level by means of water or mist ejected from nozzles 9. The web may be treated with water spraying or steam injection also before it passes over the rolls. In the embodiment shown in Fig. 4, the adherence of the coating is enhanced by means of electromagnetic radiation. The radiation emitter is denoted by reference numeral 20 and the type of radiation applied may be infrared, ultraviolet, radioactive or x-ray radiation or microwave energy. A particularly advantageous technique is to combine the application of radiation with web treatment by a chemical responsive to the radiation used. Such treatment chemicals can be applied to the web in the above-described manner either in front of or after the ion-blast chamber. In Fig. 5 is shown a simplified embodiment of the invention, in which the nano-size coating particles are adhered to the web and each other by van der Waals forces alone without using any other treatments.

In Fig. 6 is shown a method and apparatus for forming a carbonate coating layer directly from precursors on the surface of the web 11. In this method, the ion-blast chamber 21 with its coating particle circulation and the structure of the conducting support belt are similar to those of the above-described apparatuses. The difference herein is that the particle circulation in the present case is fed with slaked lime particles  $\text{CaO}$  that are transferred to the web surface by ion-blasting. Next, the web is passed into an enclosure 24 where water is applied to the web, e.g., under a steam or mist atmosphere. Alternatively, the water may be introduced as mist or steam in the ion-blast chamber 21 or using any other suitable technique. When the slaked lime  $\text{CaO}$  reacts with the applied water, calcium hydroxide  $\text{Ca(OH)}_2$  is formed. Next, the web 11 is passed into a chamber enclosing a carbon dioxide atmosphere partially or purely comprised of carbon dioxide, whereby the calcium hydroxide  $\text{Ca(OH)}_2$  reacts with the carbon dioxide so as to form calcium carbonate particles on the web surface. The water released in the reaction is discharged from the chamber. When desired, the adherence of the formed particles to the web surface may be secured by ion-blasting, whereby also a blast of carbon dioxide gas can be directed to the web surface.

Alternatively, a blast of powdered calcium hydroxide may be directed to the web surface, whereby the reaction described above is effected under a carbon dioxide atmosphere. Again, the applied powdered material and the carbon dioxide gas can be directed to the web and adhered thereto by means of ion-blasting. Further alternatively, the calcium hydroxide may be introduced to the web surface as an aqueous solution by spraying from jet nozzles, whereby the required carbon dioxide can be blown along with the atomizing air of the jet nozzles via orifices

made to the jet nozzles. In the latter case, the reaction forming the calcium carbonate occurs partially airborne and partially on the web surface. When using particulate PCC, the agglomeration of the formed particles can be  
5 impeded by introducing external energy in the manner described, e.g., in conjunction with the discussion above related to Fig. 4. To enhance the adherence of the particles, the surface charge states of the paper web fibers may be altered by various physical or chemical  
10 treatments using, e.g., alum, polymer, electrolytic or corona discharge treatments and altering the pH level of the process. The coating structures thus formed may be processed further using the above-mentioned types of treatments and mechanical treatments such as calendering.

15

In addition to those described above, the present invention may have alternative embodiments.

The coating material consisting of nano-size PCC that was  
20 used in dry-coating tests is formed in a gas phase without a slurring step in an aqueous medium. The native particles are in amorphous form and their crystallization takes at least some seconds or minutes. In its amorphous form, the workability of the material is much better than  
25 that of a crystalline material. However, after some time the material undergoes crystallization and the workability of the material decreases which means that its stiffness increases. This phenomenon may be utilized in the surface treatment of a paper or board web. In tests per-  
30 formed, it has been found that the nano-size PCC is not in crystallized form directly after the coating process, but after some time the crystallization of the particles can be seen as scattering points under a microscope.

35 In its amorphous form, that is, immediately after the carbonization of calcium hydroxide, the applied coating is readily workable. Hence, the nano-size PCC should be

calendered or otherwise smoothed immediately after the application. Then, the calendering effect is imposed on the readily workable amorphous, cloudberry-like calcium carbonate aggregates (nano-size PCC). The aggregates are  
5 durable under the plastic deformation and can be levelled under the calendering pressure to form a smooth surface. Also the individual aggregates undergo a plastic deformation. Resultingly, a surface with an extremely smooth and level profile is obtained. The levelling of the web sur-  
10 face to a smooth profile immediately after application may be implemented using the following techniques:

a) cold calendering involving mechanical compaction, whereby the fixation of the aggregate particles may also require the use of a specific binding agent if the  
15 bonding forces between the fibers of the base web and the coating particles are not sufficiently strong to ensure so strong bonds that the coating material can adhere in a secure manner to the web surface;

b) hot calendering in which the water contained in the  
20 aggregate particles is released during hot calendering under the hot calender roll thus improving the formation of hydrogen bonds between the aggregate particles of the coating material (this does not exclude the use of bond-formation-promoting additives) and the paper web, as well  
25 as the formation of interparticle bonds. The test results of this latter technique have been positive.

In Fig. 7 is shown a further embodiment of the invention suited for exploiting the above-described phenomenon.  
30 Herein, the coating is applied to the web 11 by means of an applicator 26 using any of the above-described techniques. Next after the applicator 26 is placed a calender in which the roll 27 facing the coated side of the web or the roll 28 facing the uncoated side of the web or even  
35 both rolls are hot rolls. In addition to the hot rolls, steam or treatment chemicals may be applied to the web, before or after the coat application. Calendering is



carried out immediately after application while the PCC is still in its amorphous state. As mentioned above, the coating material particles are amorphous when leaving the carbonization process. The coat application step may be

5      complemented with binding agents, polymers, advantageously resins, latexes or natural binding agents that enhance the forces adhering the coating material particles to the paper web and bind the particles to each other. PCC aggregates are durable under the plastic

10     deformation and can assume a smooth surface structure under the contact pressure of calendering. Also the individual aggregate particles are deformed. To avoid crystallization prior to calendering, the delay time from coat application to calendering must be sufficiently

15     short. Since this delay time  $t$  is dependent on the properties of the PCC used, the web travel distance from the applicator to the calender is advantageously made adjustable so that the instant of calendering with regard to the progress of crystallization can be controlled.

20     Under normal operating conditions, however, the time of crystallization is so long that the calendering must invariably be carried out while the coating is still in its clearly amorphous state.

25     In dry-coating tests performed, the paper web has been subjected to abrasion with a mechanical brush that fibrillates the web surface thus improving the adherence of coating material particles to the surface structure of the fiber matrix. The principle of the fibrillation

30     handling is shown in Fig. 8. In this technique, the surface of the web 11 is abrasively treated with a brush 29 made from a suitable material, whereby microfibrils 30 are elevated from the fibers of the web. As known, rubbing of two dielectric materials against each other,

35     e.g., by brushing movements creates static electricity. In this manner, charging of a dry paper web with static electricity is relatively easy. Since dry paper falls

midway on the scale of dielectric materials by its tribo-electric properties, suitable brush materials are readily available for charging a paper web with positive or negative static electricity. This technique may be applied to  
5 alter the properties of a paper web surface, e.g., for a subsequent ion-blast treatment.

Web surface fibrillation by brushing improves the adherence of coating material particles by:

- 10 a) increasing the specific surface area (through fibrillation)
- b) increasing the coarseness of the web surface
- c) generating static electricity.

15 During brushing, the surface of a paper web to be dry-coated is fibrillated in brushing pretreatment step (by separating the fibrils of the walls of the most superficial fibers of the fibrous web matrix so much that their one end remains attached to the basic fiber while  
20 the other end of the fibril remains hanging free).

The degree of surface-fibrillation can be controlled by altering the rotational speed of the brush and using different brushing pressures. The brush may be rotated  
25 along or reverse to the web travel. The paper web surface can be charged with static electricity by selecting the brush material so that a desired polarity, that is, positive or negative charge, is generated on the web surface. Analogously, the amount of static electricity  
30 generated herein can be controlled by altering the rotational speed of the brush and using different brushing pressures. Also analogously, the brush may be rotated along or reverse to the web travel.

35 While the use of calcium carbonate aggregate particles alone for treating a moving web is described in the foregoing examples, also other types of pigment particles may

be used such as silicates, plastic pigments titan oxide and other mineral based pigments. However, the particle size under all conditions must be so small that the interparticle and particle-to-web adherence can be accomplished by van der Waals forces, possibly augmented with ion and hydrogen bonds serving to bond the fibers together with each other. The average size of the pigment particles should be in the range of 0.5 - 100 nm, advantageously 15 - 25 nm. The flocced cloudberry-like aggregates of particles should have an average diametral size of less than 500 nm, advantageously less than 100 nm. If the pigment particles are applied in dry form, the solids of the applied coating should preferably be greater than 80 %.

In FI Pat. Appl. No. 973775 is disclosed a method of forming a paper or board web or any other web of basically fibrous structure, in which method a moving web-formation substrate is covered with a raw material furnish comprising cellulosic pulp fiber, plant fiber or other materials suitable for making a paper, board or nonwoven product. The raw material furnish fed onto the web-formation substrate is passed into at least one compression nip for forming a firm web from the laid fibers of the raw material. Next, the web-formation substrate is connected to a first electrical potential and a second potential higher than said first potential is applied displaced from said first potential at a distance above that side of the web-formation substrate on which the raw material furnish is being fed, whereby an electric field is established between said potentials. The voltage between said first potential and said second potential is adjusted so high as to establish a corona discharge in the vicinity of said higher potential, said discharge being capable of causing an ion blast from said higher potential to said lower potential, whereby said ion blast transports the particulate raw material exist-

ing in the space between said potentials onto said web-formation substrate and assures the adherence of the raw material to the substrate. In conjunction with the above-described method, the particles of web treatment material  
5 can be fed in the web-formation step into the flow of the raw material fibers or, alternatively, directly onto the formed web in a manner described above.

In addition to a conducting wire or replacing the same,  
10 the counter electrode of the ion-blast apparatus may comprise a conducting belt, possibly a plurality of belts, and in special cases, a roll or set of rolls, provided that such an arrangement can offer a sufficiently long distance of web travel for applying the raw  
15 material. Also a construction with a nonconducting wire may be contemplated having at least one counter electrode placed under such a wire.

A product made according to the invention is characterized by having microscopic particles of the above-  
20 described mineral origin, advantageously small calcium carbonate particles, applied on its surface and/or in its interfiber spaces.

What is claimed is:

1. Method for making a web of paper or board, the method comprising the steps of:

5

- forming a web (11) from fibers, and
- treating the web (11) with pigment particles,

10 c h a r a c t e r i z e d in that the web is treated with particles having an average size in the range of 0.5 - 100 nm, most advantageously 15 - 25 nm.

15 2. Method according to the claim 1, c h a r a c t e r - i z e d in that, that the web is treated with such elementary pigment particles that have an average size sufficiently small to bind the particles together at least by van der Waals forces.

20 3. Method according to claim 1, c h a r a c t e r - i z e d in that the web is treated with calcium carbonate particles ( $\text{CaCO}_3$ ).

25 4. Method according to claim 3, c h a r a c t e r - i z e d in that the web is treated with particles comprised essentially of single elementary particles.

30 5. Method according to claim 3, c h a r a c t e r - i z e d in that the web is treated with flocced particles comprised of elementary particles.

6. Method according to claim 1, c h a r a c t e r - i z e d in that the web is treated with flocced particles having an average size not larger than 500 nm.

35

7. Method according to claim 5 or 6, c h a r a c - t e r i z e d in that the size of the flocced particles

comprised of the elementary particles is controlled by arranging turbulent conditions for the particle flow and then controlling the degree of turbulence in the flow.

- 5 8. Method according to claim 5 or 6, c h a r a c -  
t e r i z e d in that the size of the flocced particles  
comprised of the elementary particles is controlled by  
adjusting the pH level of the particle surroundings.
- 10 9. Method according to claim 1, c h a r a c t e r -  
i z e d in that the particles are formed on the web  
surface by first treating the web with slaked lime ( $\text{CaO}$ ),  
then reacting the slaked lime with water in order to form  
calcium hydroxide ( $\text{Ca(OH)}_2$ ) and finally reacting the  
15 calcium hydroxide with carbon dioxide ( $\text{CO}_2$ ) in order to  
form calcium carbonate particles ( $\text{CaCO}_3$ ).
- 20 10. Method according to claim 1, c h a r a c t e r -  
i z e d in that the particles are formed on the web  
surface by first treating the web with calcium hydroxide  
( $\text{Ca(OH)}_2$ ) and then reacting the calcium hydroxide with  
carbon dioxide ( $\text{CO}_2$ ) in order to form calcium carbonate  
particles ( $\text{CaCO}_3$ ).
- 25 11. Method according to any of foregoing claims 1 - 8,  
c h a r a c t e r i z e d in that the solids content of  
the web treatment material is at least 80 %.
- 30 12. Method according to any of foregoing claims 1 - 8,  
c h a r a c t e r i z e d in that the particles of the  
web treatment material are adhered to the web surface and  
the web is treated prior to the application of the  
particles by alum, polymer, electrolytic or corona  
discharge treatments.
- 35 13. Method according to any of foregoing claims 1 - 8,  
c h a r a c t e r i z e d in that the adherence of the

particles of the web treatment material to the web surface is augmented after the application step by electromagnetic radiation treatment using, e.g., infrared, ultraviolet, radioactive, x-ray or microwave radiation.

5

14. Method according to any of foregoing claims 1 - 8, characterized in that the adherence of the particles of the web treatment material to the web surface is augmented by mechanical or thermomechanical treatment.

10

15. Method according to claim 14, characterized in that the web (11) is brushed in order to elevate microfibrils (30) of the web fiber walls up from the web surface.

15

16. Method according to claim 15, characterized in that the brush material is selected so that the surface of the web (11) is charged with static electricity of negative or positive polarity as desired.

20

17. Method according to any of foregoing claims 1 - 8, characterized in that the web is calendered after the particle treatment step.

25

18. Method according to claim 17, characterized in that the web is calendered prior to the crystallization of the calcium carbonate particles from their amorphous state.

30

19. Method according to claim 18, characterized in that at least one of the calender rolls (27, 28) is a hot roll.

35

20. Method according to claim 18, characterized in that the web (11) is treated with a treatment material prior to calendering.

21. Method for forming a web of paper or board or any other chiefly plant-fiber-based web, said method comprising the steps of

5

- spreading on a moving web-formation substrate (1) such web-forming raw material that contains cellulosic fiber, plant fiber or other material suitable for manufacturing a paper, board or nonwoven product.

10

- feeding the raw material on said web-formation substrate (1) and travelling thereon into at least one compressive nip (1, 5, 11, 12) in order to form a firm web from the fibers of said raw material,

15

c h a r a c t e r i z e d   i n   t h a t

- bringing said web-formation substrate (1) to a first electrical potential,

20

- applying a second potential higher than said first potential and displaced from said first potential at distance above that side of the web-formation substrate (1) on which the raw material furnish is being fed, whereby an electric field is established between said potentials,

25

- adjusting the voltage between said first potential and said second higher potential so high as to establish a corona discharge in the vicinity of a point brought to said second higher potential, said discharge being capable of causing an ion blast from said higher potential to said lower potential, whereby said ion blast transports the particulate raw material existing in the space between said potentials onto said web-formation substrate (1) and assures the adherence of the raw material to the

30

35



substrate (1), and

- treating the web with elementary pigment particles having an average size in the range of 0.5 - 100 nm, most advantageously 15 - 25 nm.

22. Method according to claim 21, characterized in that the treatment material particles are added to the web at least during the web formation step, whereby the particles form interfiber bonds at least by van der Waals forces.

23. Method according to claim 21 or 22, characterized in that the treatment material particles are added to the surface of the formed web.

24. Method according to claim 23, characterized in that the treatment material particles are added to the surface of the formed web by means of an ion-blast technique.

25. Method according to claim 21, characterized in that the web is treated by adding the particles to the web surface by first treating the web with slaked lime ( $\text{CaO}$ ), then reacting the slaked lime with water in order to form calcium hydroxide ( $\text{Ca(OH)}_2$ ) and finally reacting the calcium hydroxide with carbon dioxide ( $\text{CO}_2$ ), whereby calcium carbonate particles ( $\text{CaCO}_3$ ) are formed.

26. Method according to claim 21, characterized in that the web is treated by adding the particles to the web surface by first treating the web with calcium hydroxide ( $\text{Ca(OH)}_2$ ) and then reacting the calcium hydroxide with carbon dioxide ( $\text{CO}_2$ ), whereby calcium carbonate particles ( $\text{CaCO}_3$ ) are formed.

27. Method according to any of foregoing claims 21 - 26, characterized in that the particles of the web treatment material are adhered to the web surface and the web is treated prior to the application of the particles by alum, polymer, electrolytic or corona discharge treatments.

28. Method according to any of foregoing claims 21 - 26, characterized in that the adherence of the particles of the web treatment material to the web surface is augmented after the application step by electromagnetic radiation treatment using, e.g., infrared, ultraviolet, radioactive, x-ray or microwave radiation.

29. Method according to any of foregoing claims 21 - 26, characterized in that the adherence of the particles of the web treatment material to the web surface is augmented by mechanical or thermomechanical treatment.

30. Method according to claim 29, characterized in that the web (11) is brushed in order to elevate microfibrils (30) of the web fiber walls up from the web surface.

31. Method according to claim 30, characterized in that the brush material is selected so that the surface of the web (11) is charged with static electricity of negative or positive polarity as desired.

32. Method according to any of foregoing claims 21 - 26, characterized in that the web is calendered after the particle treatment step.

33. Method according to claim 32, characterized in that the web is calendered prior to the

crystallization of the calcium carbonate particles from their amorphous state.

34. Method according to claim 33, c h a r a c t e r -  
5 i z e d in that at least one of the calender rolls  
(27, 28) is a hot roll.

35. Method according to claim 33, c h a r a c t e r -  
i z e d in that the web (11) is treated with a treatment  
10 material prior to calendering.

36. Method according to any of foregoing claims 21 - 26,  
c h a r a c t e r i z e d in that the web is treated  
with recycled calcium carbonate obtained from the  
15 precipitated calcium carbonate residue of the deinking  
process of recycled fiber.

37. Method according to claim 36, c h a r a c t e r -  
i z e d in that the calcium carbonate is prepared by  
20 calcining calcium-carbonate-containing precipitate into  
lime, reacting the lime with water and reacting the  
calcium hydroxide thus formed with carbon dioxide in a  
turbulent gas phase, whereby fine particulate calcium  
carbonate is formed.

25 38. Assembly for making a web of paper or board contain-  
ing calcium carbonate, the assembly comprising:

- means (12 - 15) for supporting a web (11) being  
30 formed, and

- means (1 - 7, 21 - 25) for forming calcium carbo-  
nate at least on the surface of said web (11),

35 c h a r a c t e r i z e d in that said means for forming  
calcium carbonate comprise at least:

- means (22) for feeding calcium hydroxide into contact with the surface of said web (11), and

5       - a chamber (22) via which said web (11) is adapted to travel and into which chamber is passed carbon dioxide containing gas in order to react carbon dioxide with calcium hydroxide so as to form calcium carbonate.

10       39. Assembly according to claim 38, c h a r a c t e r - i z e d in that said means for feeding calcium hydroxide into contact with the surface of said web (11) comprise at least means (1 - 7, 21 - 23) for applying slaked lime on the surface of said web (11) and means (21) for  
15       reacting said slaked lime with water in order to form calcium hydroxide.

20       40. Assembly according to claim 38, c h a r a c t e r - i z e d in that said means for feeding calcium hydroxide on the surface of said web (11) comprise gas-atomizing liquid jet nozzles in which calcium hydroxide solution is sprayed via the nozzle jet orifice and carbon-dioxide-containing gas is discharged via the atomizing orifices of the nozzle, whereby the reaction between said two  
25       components forms calcium carbonate.

30       41. Assembly according to claim 38, c h a r a c t e r - i z e d in that said means for feeding slaked lime on the surface of said web (11) comprise:

35       - means (1, 2, 3, 21) for feeding mineral-based materials or other furnish required in the making of a paper or board web or a nonwoven product onto the surface of a web (11) travelling on support means,

- at least one connection (16) for applying a first electrical potential to said web-supporting means

(12 - 15) thus forming a first electrode,

- at least one second electrode (22) disposed at a distance from said web-supporting means (15) forming said first electrode, and

- a high-voltage supply (23) for elevating the voltage between said first electrode (15) and said at least one second electrode (22) so high that as to establish a corona discharge in the vicinity of said second higher-potential electrode (22), said discharge being capable of causing an ion blast from said second higher-potential electrode (22) to said first lower-potential electrode (15), whereby said ion blast transports the particulate raw material existing in the space between said potentials (15, 22) onto said web-formation substrate (11) running on said web-supporting means (15) and assures the adherence of the raw material to the substrate (11).

42. Assembly according to claim 41, characterized by

- an ion-blast chamber (21) via which the moving web (11) being treated is adapted to pass and into whose interior said at least one second electrode (22) is disposed, and,

- means (3) for keeping said treatment material of microscopic particles in a continuous turbulent motion at least within the interior of said ion-blast chamber.

43. Assembly for treating a paper or board web with a treatment material, said assembly comprising:

- an electrically conducting moving wire (15) having

a first surface and a second side on reverse side to said first side, said wire being adapted to support said web (11) to be treated, and

- 5       - means (1 - 7, 21 - 23) for feeding said treatment material containing mineral-based components onto said web (11) travelling on said first surface of said moving wire (15),

10     c h a r a c t e r i z e d   b y

- at least one first electrode (15) for forming a first potential field on said second side of said wire (15),

15

- at least one second electrode (22) disposed at a distance from the first side of said wire forming said first electrode, and

20

- a high-voltage supply (23) for elevating the voltage between the first electrode potential (16) and said at least one second electrode (22) so high that as to establish a corona discharge in the vicinity of said second higher-potential electrode (22), said discharge being capable of causing an ion blast from said second higher-potential electrode to said wire (15) forming said first electrode of said lower potential (16), whereby said ion blast transports the particles of said web-treatment material existing in the space between said potentials onto said web (11) and assures the adherence of the raw material to the web (11).

25

30

35

44. Assembly according to claim 43, c h a r a c t e r -  
i z e d   b y

- an ion-blast chamber (21) via which the web (11)

being treated is adapted to pass and into whose interior said at least one second electrode (22) is disposed, and,

5        - means (3) for keeping said treatment material of microscopic particles in a continuous turbulent motion at least within the interior of said ion-blast chamber (21).

10       45. Assembly according to claim 44, c h a r a c t e r - i z e d in that said means for keeping said treatment material in a continuous turbulent motion comprise a particle circulation tube (3) adapted to perform in the ion-blast chamber as a return circulation path via which  
15       said treatment material can be fed into said ion-blast chamber (21) and via which the fraction of the material not adhering to the web can be removed and returned back to the ion-blast chamber and further serving to keep the particles of the treatment material in continuous motion  
20       so that said particles form aggregate particles of a desired size.

46. Assembly according to any of foregoing claims  
25       43 - 45, c h a r a c t e r i z e d by means (9, 17) for treating said web (11) prior to the application of the particles by alum, polymer, electrolytic or corona discharge treatments.

47. Assembly according to any of foregoing claims  
30       43 - 45, c h a r a c t e r i z e d by means (20) for augmenting the adherence of the particles of the web treatment material to the surface of said web (11) after the application step by electromagnetic radiation treatment using, e.g., infrared, ultraviolet, radio-  
35       active, x-ray or microwave radiation.

48. Method according to any of foregoing claims 43 - 45,

c h a r a c t e r i z e d by means (19) for augmenting the adherence of the particles of the web treatment material by mechanical or thermomechanical treatment.

5 49. Assembly according to claim 48, c h a r a c t e r - i z e d by at least one brush for elevating microfibrils (30) from the web surface.

10 50. Assembly according to claim 49, c h a r a c t e r - i z e d in that the brush material is selected so that the surface of the web (11) under a treatment with the brush material is charged with static electricity of negative or positive polarity as desired.

15 51. Method according to any of foregoing claims 43 - 45, c h a r a c t e r i z e d by a calender disposed after the particle treatment step downstream in the travel direction of the web (11).

20 52. Method according to claim 51, c h a r a c t e r - i z e d in that the distance between said calender (27, 28) and the application point (26) of said web coating material particles is selected so that the web can be calendered prior to the crystallization of the calcium  
25 carbonate particles from their amorphous state.

53. Method according to claim 52, c h a r a c t e r - i z e d in that at least one of the calender rolls (27, 28) is a hot roll.

30

54. Method according to claim 52, c h a r a c t e r - i z e d by means for treating said web (11) with a treatment material prior to calendering.

35 55. Paper, board or nonwoven product comprising a fiber layer containing cellulosic fiber, plant fiber or other material suitable for manufacturing a paper, board or



nonwoven product, characterized by having at least one surface of said fiber layer treated with elementary pigment particles of size in the range of 0.5 - 100 nm, most advantageously 15 - 25 nm.

5

56. Product according to claim 55, characterized in that said particles contain at least calcium carbonate.

10

57. Product according to claim 55, characterized in that said product contains particles of such an average size that they adhere to each other by van der Waals forces.

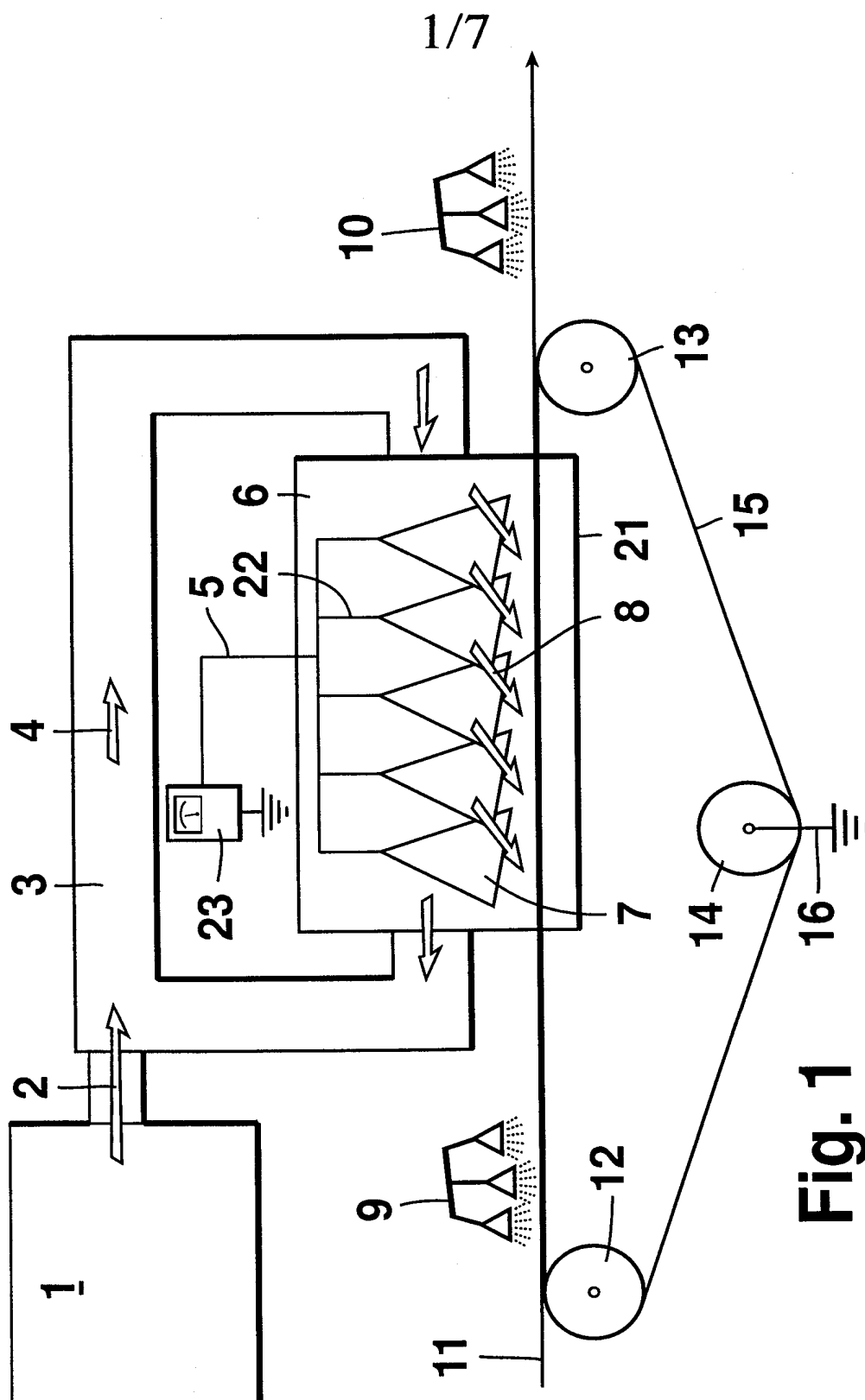
15

58. Product according to claim 55 or 56, characterized in that said particles are also introduced between the web fibers, whereby the particles are bonded to the fibers by at least van der Waals forces and act so as to bond the fibers to each other.

20

59. Use of recycled calcium carbonate in the treatment of a paper, board or nonwoven product, said calcium carbonate being prepared by calcining the precipitated calcium carbonate residue of the deinking process of recycled fiber into lime, reacting the lime with water into calcium hydroxide and reacting the calcium hydroxide thus formed with carbon dioxide into calcium carbonate so that particles can be formed having an average particle size so small as to permit the particles to adhere to each other by van der Waals forces.

30



1/7

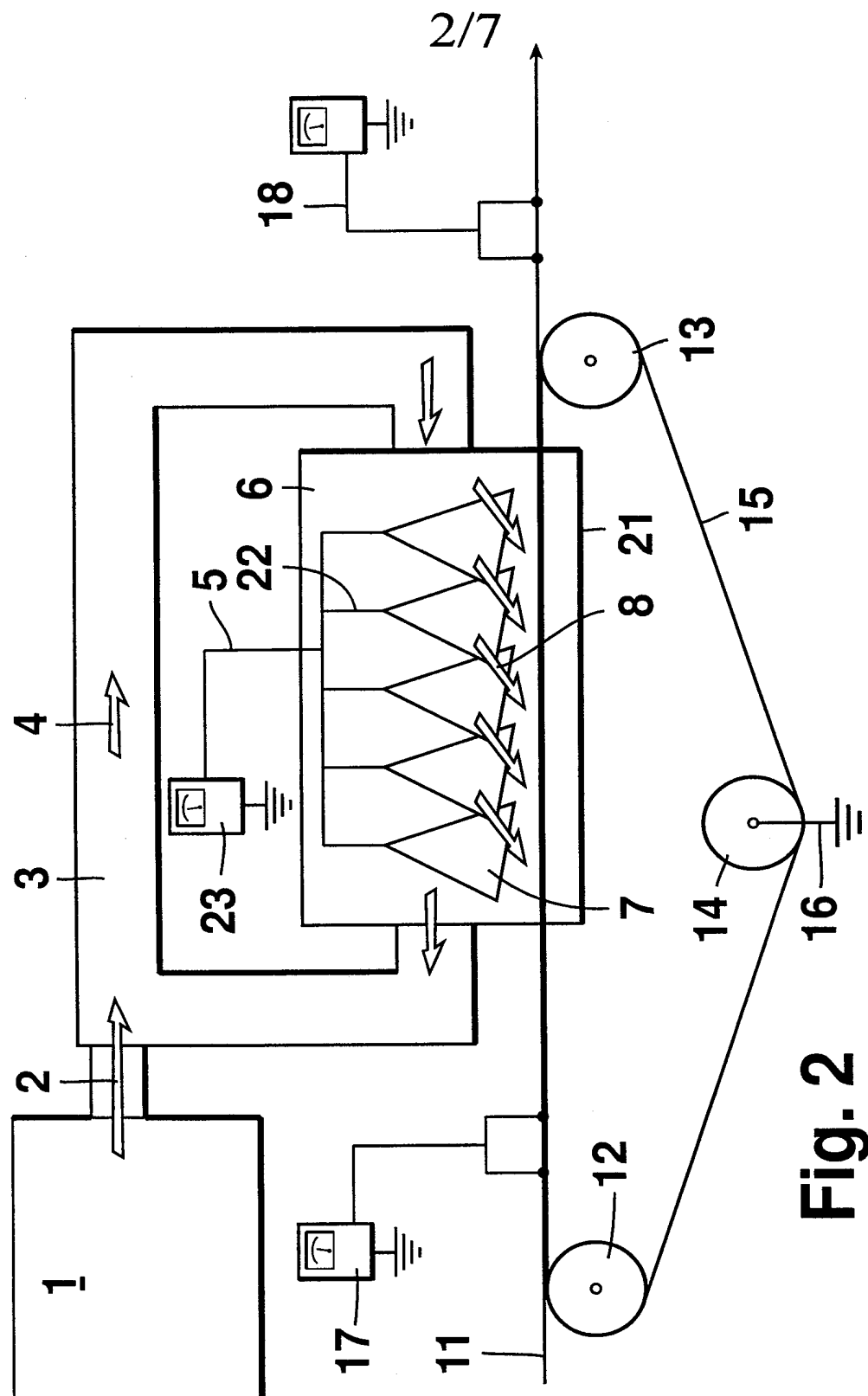


Fig. 2

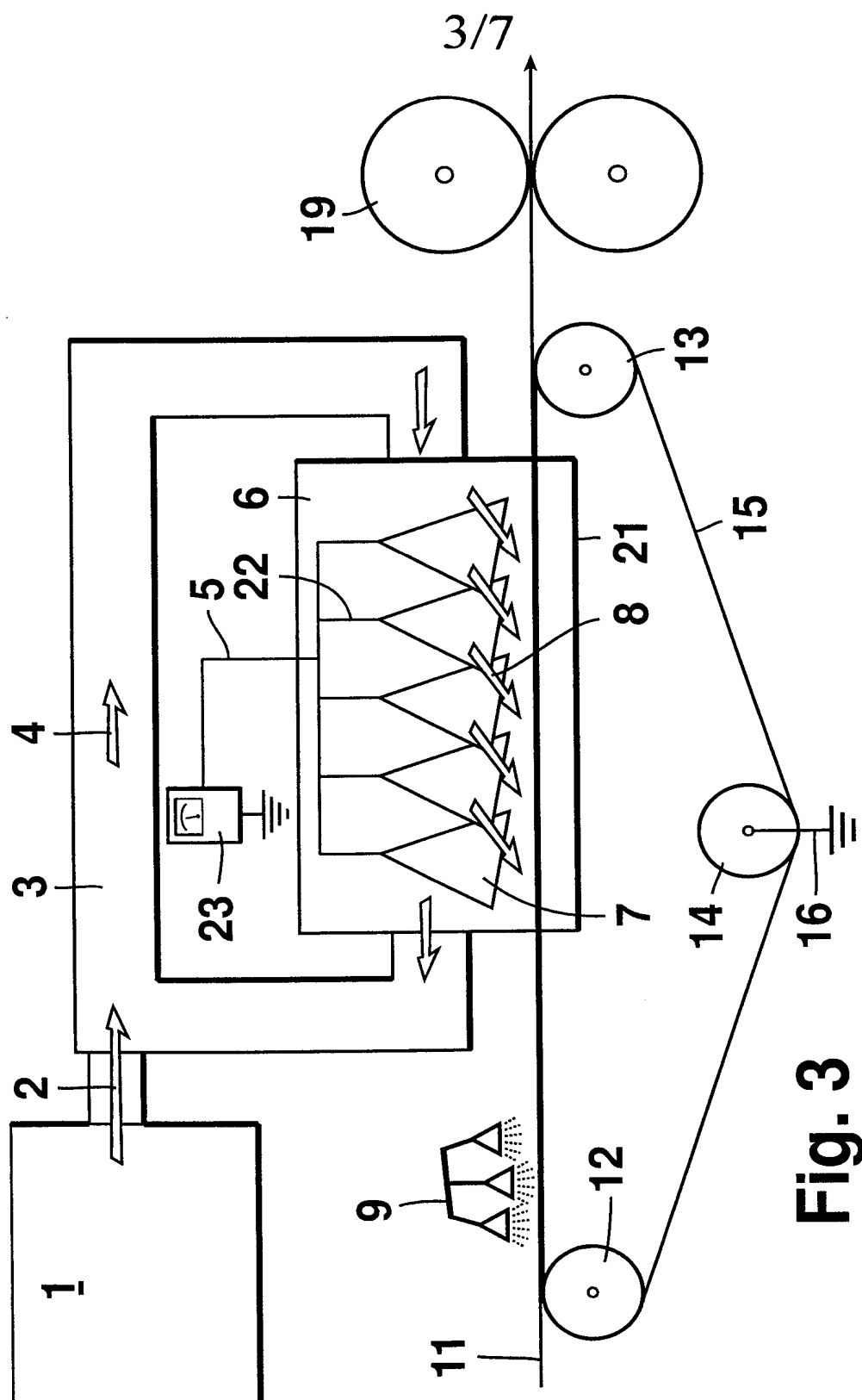


Fig. 3

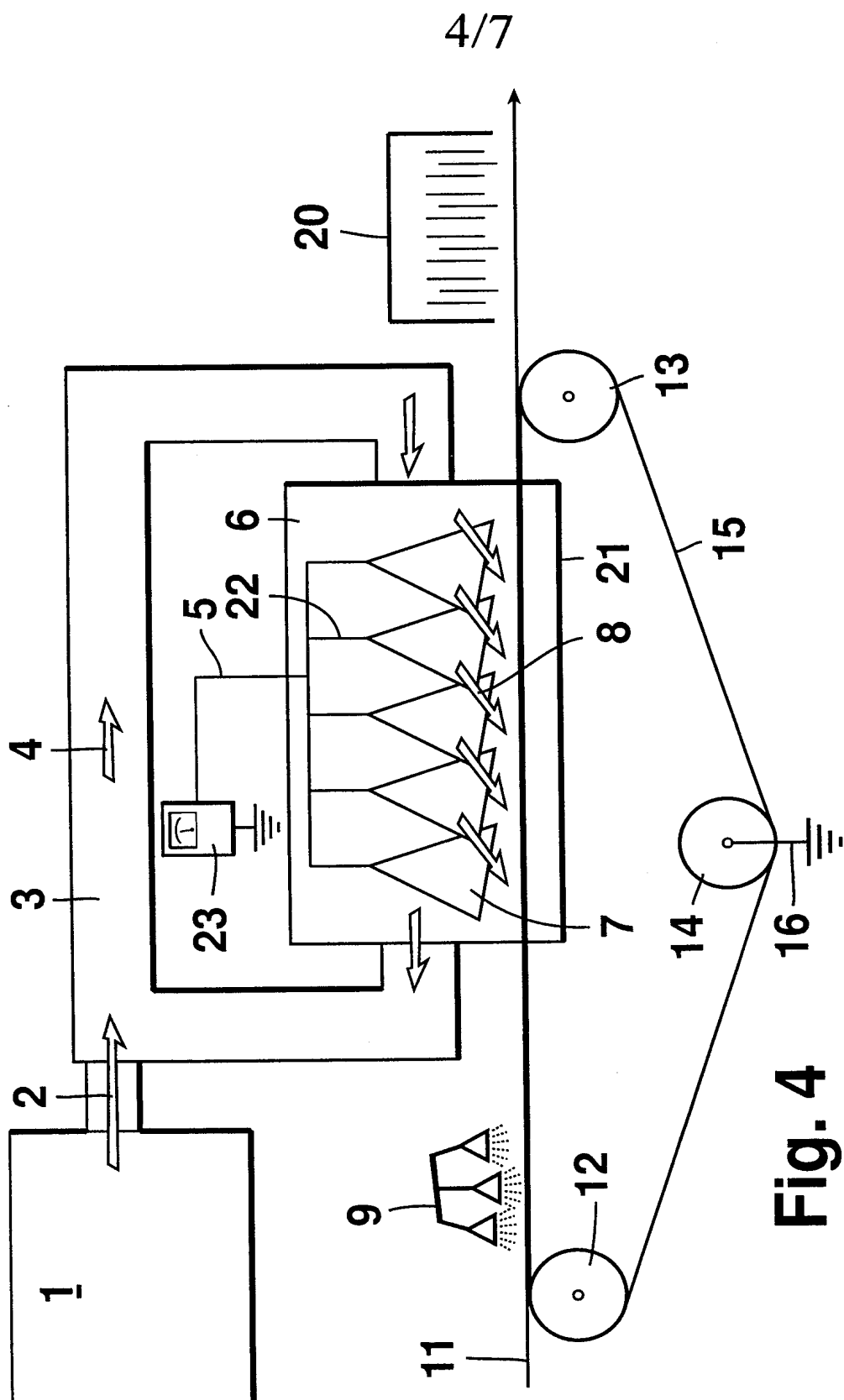


Fig. 4

5/7

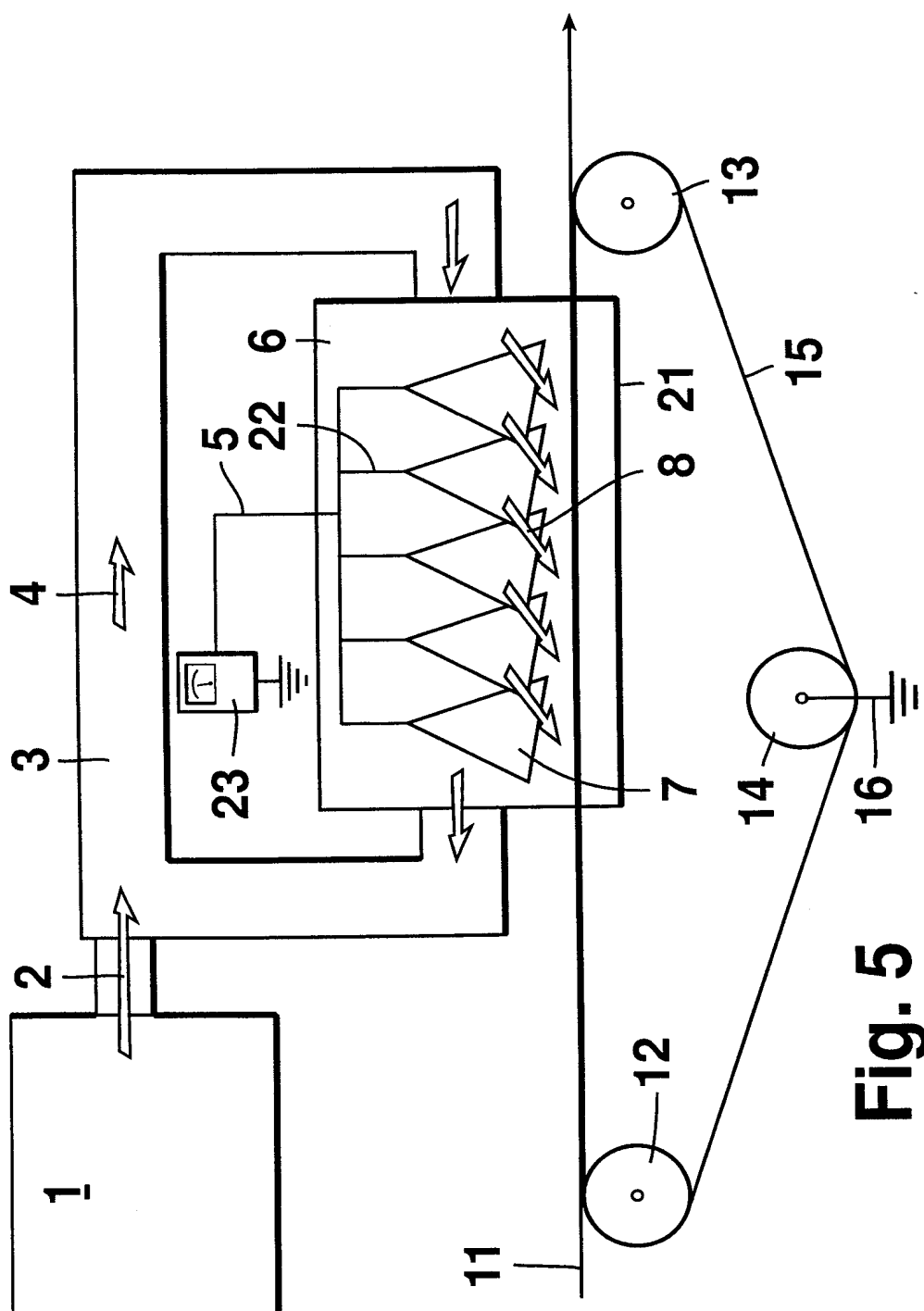


Fig. 5

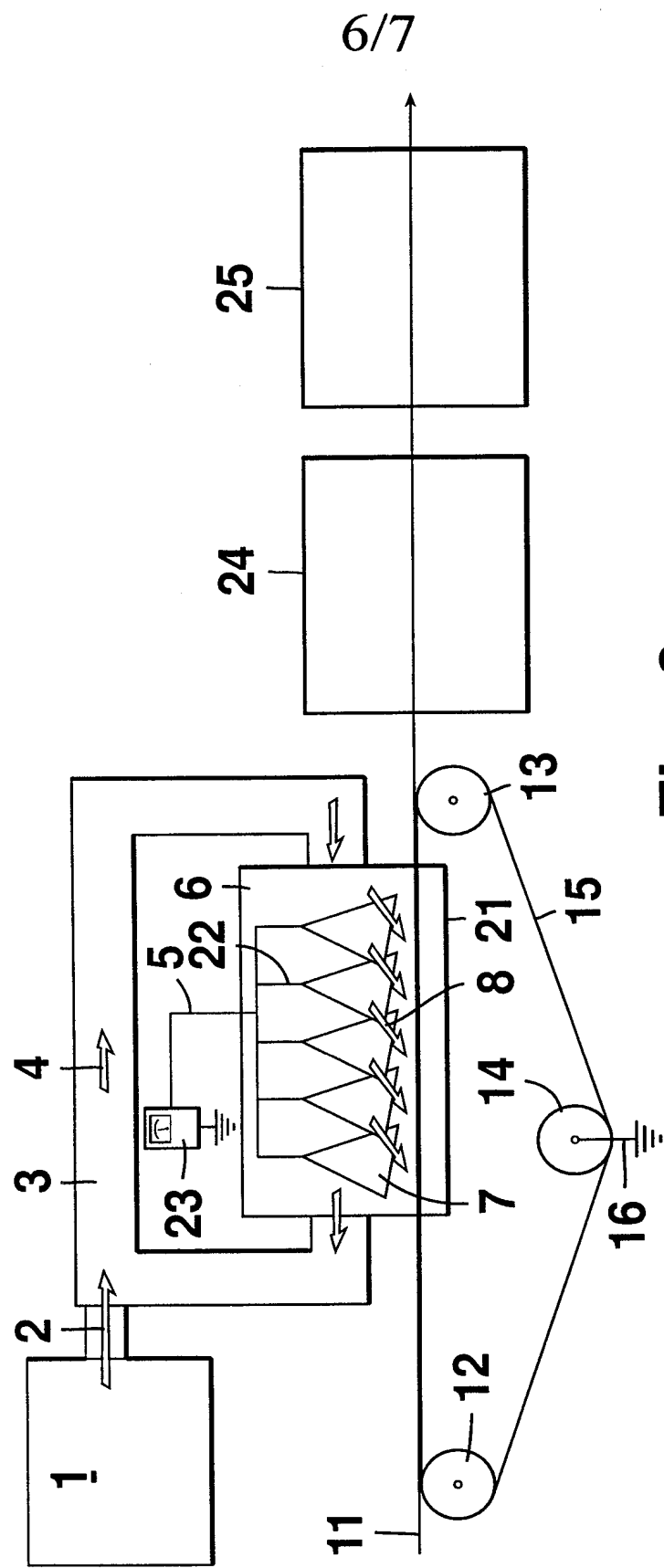


Fig. 6

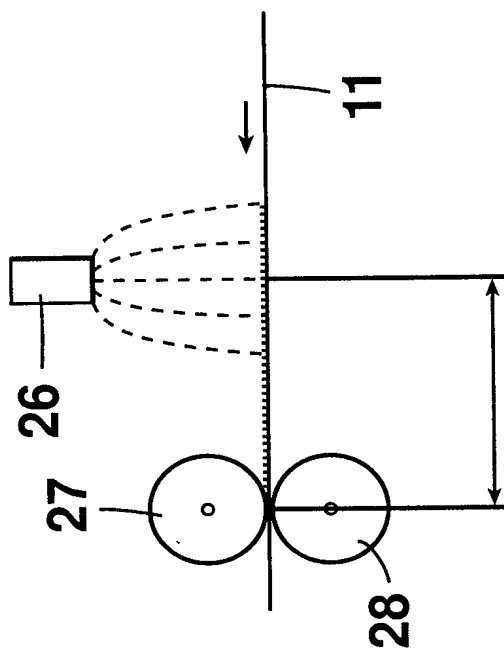


Fig. 7

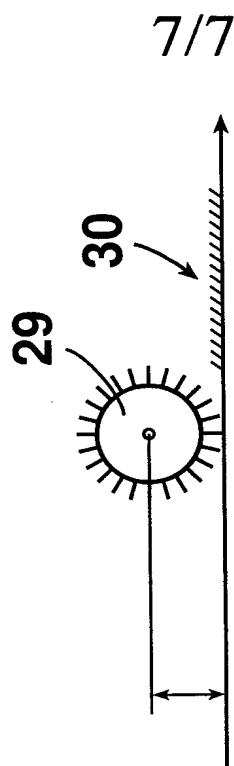


Fig. 8



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 99/00604

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21H 17/67, D21H 19/36, D21H 23/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9732934 A1 (KAUTAR OY), 12 Sept 1997 (12.09.97), abstract; claims 1-6, 10; page 3, lines 1-9; page 5, lines 1-3  --	1-8
A	US 4133894 A (HIROJI SHIBAZAKI ET AL), 9 January 1979 (09.01.79), claim 1  --	1-59
X	WO 9518885 A1 (F.L. SMIDTH & CO. A/S), 13 July 1995 (13.07.95), abstract; claims 1-6; page 7, lines 17-31  -- -----	59

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 November 1999

Name and mailing address of the ISA /

Swedish Patent Office  
Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Date of mailing of the international search report

04 -11- 1999

Authorized officer

Barbro Nilsson/EÖ

Telephone No. +46 8 782 25 00

# INTERNATIONAL SEARCH REPORT

Information on patent family members

28/09/99

International application No.

PCT/FI 99/00604

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9732934 A1	12/09/97	AU 706130 B AU 2097197 A CA 2247968 A CN 1217007 A FI 961003 A FI 964365 A	10/06/99 22/09/97 12/09/97 19/05/99 05/09/97 30/04/98
US 4133894 A	09/01/79	DE 2742829 A,B,C DE 2759551 B,C FR 2378720 A,B GB 1530080 A JP 995924 C JP 53039998 A JP 54027200 B	30/03/78 19/02/81 25/08/78 25/10/78 30/04/80 12/04/78 08/09/79
WO 9518885 A1	13/07/95	AU 1310995 A EP 0738346 A	01/08/95 23/10/96